Organic contaminants and metals in water, sediment and sludge samples from two hydraulic fracturing sites in Argentina – a briefing.

Summary

- Samples of water and sediment have been analysed for concentrations of metals, organic chemicals and petroleum hydrocarbons. The full report can be found here.
- In most cases the concentration of metals were not significantly higher than the average found naturally, although four samples had higher levels of barium and strontium; one sample, from the cutting repository, also had higher concentrations of cadmium and lead.
- The water samples did not have higher concentrations of metals than found naturally and did not have significant levels of semi-volatile or volatile organic compounds.
- Many of the sediment samples, however, had extremely high concentrations of hydrocarbon chemicals; one was too contaminated to be analysed in detail.
- Four of the five sediment samples that could be analysed for Extractable Petroleum Hydrocarbons (EPH) had much higher levels than that considered 'normal' for uncontaminated environmental samples. The presence of such high levels justifies further investigation and remedial action to reduce the level of contamination.
- The samples collected from waste repositories had higher levels of hydrocarbon pollution than thresholds that have been applied in other countries to assess contaminated soils. These wastes have nevertheless been placed directly on soil in open and poorly controlled conditions that raises serious concerns for the potential contamination of the air, soil, surface waters and groundwater.
- More detailed surveys are urgently needed to determine whether these oily wastes are contaminating the surrounding environment.
- The concentrations of hydrocarbons in these samples are so high that they should be handled through proper containment, treatment and disposal, rather than by simple evaporative storage in open ponds.
- The waste materials, collected from easily accessible open sites, are clearly highly contaminated, with the potential to generate odour nuisance, fire risk and possible health risks for local communities and wildlife.

Introduction

In May this year a Greenpeace team investigating the impact of oil and gas developments in and around the City of Neuquen in northern Patagonia took samples of water and sediment for chemical analysis. The samples were analysed at the Greenpeace Research Laboratories at Exeter University in the UK and another independent laboratory. The details of the sampling, analysis and the results can be found in the report here. The details of where the samples were taken can be seen in Table 1.

Table 1: The samples received and analysed at the Greenpeace Research Laboratories.

Sample code	Sample type	Date & time	Location	Analyses conducted
VM18001	Fresh water (pumped from Well)	**14:00, 17.05.2018**	Tratayen, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18002	Sludge (from an abandoned sludge	**18:12, 17.05.2018**	Calera, Neuquen,	metals (quantitative), sVOCs & VOCs

	repository)		Argentina	(screening, qualitative)
VM18003	Sediment (Dirt from a water/chem spill site)	**13:30, 18.05.2018**	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
				Extractable Petroleum Hydrocarbons /EPH (quantitative)
VM18004	Sediment (Dirt from a water/chem spill site)	**13:35, 18.05.2018**	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
				EPH (quantitative)
VM18005	Water (from a channel next to a School)	**15:00, 18.05.2018**	South Allen, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18006	Fresh water (Community's drinkable water)	**15:50, 18.05.2018**	Costa Blanco, Rio Negro, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
VM18007	Sediment (from an abandoned cutting repository)	**17:48, 19.05.2018**	Loma de la Lata, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
				EPH (quantitative)
VM18008	Sediment (from an abandoned cutting repository)	**17:55, 19.05.2018**	Loma de la Lata, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
				EPH (quantitative)
VM18009	Sediment (from an active cutting repository)	**19:40, 19.05.2018**	Loma Campana, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)
				EPH (quantitative)
VM18010	Fresh water (Community's drinkable water)	**unknown, 20.05.2018**	Campo Maripe, Neuquen, Argentina	metals (quantitative), sVOCs & VOCs (screening, qualitative)

Materials and methods

The samples were analysed for concentrations of toxic materials such as metals, volatile organic chemicals and petroleum hydrocarbons. Detailed descriptions of the sample preparation and analytical procedures can be found in Appendix 1 of the report.

Results and Discussion

The full results are in the report and appendix 2, which contains the graphs and detailed lists of organic chemicals that could be identified.

Metals

In most cases the concentration of metals in the samples were not significantly higher than the average found naturally in shale and continental rock, but there were notable exceptions that are highlighted in Table 2. Concentrations of barium and strontium in the samples from the cutting repositories were considerable higher than the natural average for shales and most other rock types. Barium compounds are commonly used as weighting agents in muds used for drilling operations. The sample from the active cutting repository also had higher concentrations of cadmium and lead than in other samples and higher than the natural average for shale and crustal rocks.

The water samples did not have higher concentrations of metals than that found in natural surface freshwaters.

Table 2: the most significant concentrations of barium, cadmium, strontium and lead metals (mg/kg DW) in the sediment and sludge samples, together with the average abundances in continental crust and in shale (Krauskopf & Bird 1994).

Sample code	VM18002	VM18003	VM18004	VM18007	VM18008	VM18009	Average abundance in continental crust [(a)]	Average abundance in shale [(a)]
Barium	272	764	372	7600	9430	7360	425	580
Cadmium	0.04	0.16	0.26	0.17	0.13	0.62	0.2	0.3
Lead	3.64	20.1	14.3	29.5	23.9	70.8	13	20
Strontium	200	213	212	10950	13800	1460	375	300

As hydrocarbon chemicals were present at extremely high concentrations in many of the samples and due to the complexity they were further investigated for organic contaminants through quantitative analysis for Extractable Petroleum Hydrocarbons (EPH). These ***organic contaminants*** - mostly come from oil or petroleum; there are two groups:

1. Volatile organic compounds or VOCs are chemicals that evaporate into the surrounding air, and;
2. Semi-Volatile organic compounds or sVOCs are chemicals with bigger molecules that don't evaporate as much; they include a group called Polycyclic Aromatic Hydrocarbons (PAHs).

Semi-volatile organic compounds (sVOCs)
The water samples did not have significant levels of semi-volatile or volatile organic compounds. However, to ensure there is no significant contamination, further samples with specialised sample bottles would be needed.

Volatile organic compounds (VOCs)
Each of the sediment samples collected from the waste repositories contained a highly complex mixture of volatile organic compounds (VOCs). One of the samples (from a repository at Loma Campana) contained a total of 183 VOCs; of those that could be reliably or more tentatively identified (119 compounds), the majority were petroleum hydrocarbons including linear hydrocarbons and their derivatives, cyclohexane derivatives, benzene derivatives and naphthalene derivatives.

Extractable Petroleum Hydrocarbons (EPH)
The analyses for Extractable Petroleum Hydrocarbons (EPH) were done by an accredited external laboratory, which measured the total concentrations of hydrocarbon chemicals including lighter and heavier oil fractions.

One sample from Calera, in Neuquen could not be analysed as it was too heavily contaminated for the equipment and methods used. The other five samples that could be analysed all contained significant levels of hydrocarbons, with by far the highest levels found in the three samples from Loma de la Lata and Loma Campana (see table 3).

Table 3: Summary of the Extractable Petroleum Hydrocarbons (EPH) quantification.

Sample Code	**VM18002**	**VM18003**	**VM18004**	**VM18007**	**VM18008**	**VM18009**

Location	Calera , Neuquen	South Allen , Rio Negro,	South Allen , Rio Negro,	Loma de la Lata , Neuquen	Loma de la Lata , Neuquen	Loma Campana, Neuquen
Sample type	Sludge	Sediment	Sediment	Sediment	Sediment	Sediment
EPH (Range > C10 - C40, mg/kg)	N.Q.?	688	78.2	59600	128000	59500

An EPH level of 100 mg/kg is often considered to be a 'normal' or background reference value for uncontaminated soils (Potra et al. 2013). Only one sample, of two from South Allen, showed hydrocarbon levels lower than this; the rest were higher and, in most cases much higher. For example, the second sample from South Allen contained 688 mg/kg EPH, indicating some past contamination with oil-related materials. Given that this sample was collected from surface soil in an apple orchard, the presence of such elevated levels justifies further investigation of possible sources and effects, as well as remedial action to reduce the level of contamination.

Solid waste samples collected from storage ponds at Loma de la Lata (VM18007 & 8) and Loma Campana (VM18009) contained far higher levels of EPH (between 59 500 and 128 000 mg/kg, or between 5.95 and 12.8% of the total weight of the sample), which indicate very high levels of hydrocarbon suggesting that these materials are wastes coming directly from industrial operations.

Regulations

It is not clear whether there are regulations or other limit values applicable to the hydrocarbon content of such wastes in Argentina, or, therefore, specific conditions or management actions that would normally be required.

Other Countries

There are examples of guidance levels or limit values for EPH in soils or wastes in certain other countries or regions, some of which have now been superseded in regulatory terms but which are nonetheless still widely used for comparative purposes.

In the Netherlands, an 'Intervention Level' for hydrocarbons in soil has been set at 5000 mg/kg (NSW EPA 2003) – EPH levels in all three samples were more than 10 times this and more than 20 times in the case of the sample from Loma de la Lata.

In the USA, some States have set screening thresholds for soils proposed for different uses; for example, in New Jersey, soils for residential use have pollution limits of 5100 mg/kg and non-residential development 54 000 mg/kg (NJAC 2012) In New Zealand the surface layers of soils in agricultural areas have limits of 4000 mg/kg (NZ MftE 2011) while residential or commercial areas have limits of 20,000 mg/kg.

All three of the samples collected from waste repositories in the current study had higher levels of hydrocarbon pollution than any of these thresholds. While we recognise that these three samples were of waste rather than soil, these wastes have been placed directly on to soil in open and poorly controlled conditions. This raises serious concerns for the potential contamination of the surrounding environment, including air, soil, surface waters and groundwater. It is urgent that more detailed surveys to determine whether the handling

and storage of these oily wastes is leading to contamination of the surrounding environment are undertaken.

The concentrations of hydrocarbons in these samples are so high that they should be handled through proper containment, treatment and disposal, rather than by simple evaporative storage in open ponds. According to UK technical guidance on classification of waste within the Europe (SEPA/NIEA/CNC/EA 2015), wastes containing petroleum hydrocarbons (TPH) at levels above 3% of the total mass would normally be required to be labelled as 'toxic to reproduction', while at greater than 10%, materials are identified as being even more acutely toxic, including through risks of inhalation/aspiration.

Irrespective of the equivalent regulations that apply in Argentina, all three of these waste materials, collected from easily accessible open sites, are clearly highly contaminated with oily residues, with the potential to generate odour nuisance and possible health and fire risk for local communities and wildlife.